IN COMPANIES AND INSTITUTES

EFFECT OF NANODISPERSE PARTICLES OF SILICON AND ALUMINUM OXIDE HYDROSOLS ON STRUCTURE FORMATION OF CLAY MINERALS IN AQUEOUS MEDIUM

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The effect of nanodisperse particles of Al and Si oxide hydrosols on structure formation of minerals in aqueous suspensions of bentonite and refractory clays was examined. The following were determined during formation of the structure of the ceramic material: pH and structure of clay suspensions, slip fluidity, shrinkage and compressive strength of samples poured from slips made of dried and thermally activated (350°C) clays.

Key words: nanodisperse particles, silicon and aluminum oxide hydrosols, aqueous suspensions of clays, properties of ceramic material.

The process stages of fabrication of ceramic items are accompanied by successive processes of alteration of structural transformations of the initial raw material, intermediate products, and final (finished) material. For this reason, the basic properties of ceramic materials are a function of both the chemical and mineralogical compositions of the raw materials and their crystal structure. The specific features of the structure of the material begin to be formed on the intermolecular level, the object of examination by nanotechnologists. The systems on this level are not equilibrium and have important internal energy which, in turn, causes the structure of the material to evolve [1, 2]. When external events (incorporation of modifiers, thermal activation, etc.) act on the material, structure formation can be affected, and this means the final properties of the material as well. We investigated some processes in this chain.

The operations for fabricating the semifinished product are based on creating and preserving the accumulative structures in the system whose energy will be used in the next stage of sintering the material. In other words, formation of the structure of a ceramic material during sintering begins from the structure of the semifinished product [1].

Most ceramic materials are molded from pastes made from aqueous-clay compositions of different moisture content, including suspensions (slips) which are widely used for ceramic casting technology. The rheological properties and aggregate stability of the slips determine their process properties and physicomechanical indexes of the finished items. Using different fluidizing additives whose effect is based on ion-exchange processes on the surface of the mineral particles in the slip is an effective method of regulating these properties. The system changes from freely disperse to structured at a certain ratio of disperse phase and dispersion medium in the suspensions [3, 4].

We know [3] that the laminar structures of clay minerals, primarily kaolinite and montmorillonite, are composed of parallel layers of silicon-oxygen tetrahedrons with aluminum, magnesium, and iron atoms basically positioned in the center. The differences in the structure of these minerals are due to the density of the crystal lattice and the distance between regularly repeating groups of ions (planes), equal to 0.72 nm for kaolinite and on average 1.5 (0.95 – 1.9 nm) for montmorillonite [5]. The greatest differences in the activity of the two minerals are due to the coordination of the aluminum ion in the structure: six-coordination in kaolinite and six- and four-coordination in montmorillonite, which is thermodynamically unstable and chemically active in montmorillonoids in the natural stage and after dehydration (thermal activation) for kaolinite. Removal of most of the water from three-layer montmorillonoid minerals causes less amorphization than in two-layer minerals of the kaolin group due to the small amount of structural hydroxides [6]. Clays with a

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TABLE 1. Composition of Clay Raw Material

Clay	Mass content, %						
	SiO_2	Al_2O_3	FeO	Fe_2O_3	CaO	MgO	$K_2O + Na_2O$
Nurlatskoe	56.4	20.0	1.13	7.0	1.61	2.78	2.0
Nizhneuvel'skoe	53.6	27.9	0.21	2.23	0.34	0.64	0.8

high content of x-ray amorphous substance are natural nanosystems, and introduction of highly disperse particles, highly concentrated ceramic binder suspensions (HCBS), for example, changes the rheological type and sedimentation stability of the system [2].

Clay-forming minerals are thus in a metastable crystalline state where the crystal lattice can be changed by different factors. It was important to verify the effect of nanosized Al and Si oxide hydrosols as basic structural elements of clay-forming minerals and thermal activation of the clays on sedimentation of clay particles in aqueous medium, and the subsequent stages of structure formation of the modified material. These effects on the raw material composition should be reflected in all stages of the production technology and final properties of the material. Using HCBS as the structure modifier could be an example of fabrication of materials with improved properties [2, 5, 6, 7, 8].
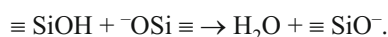
The above suggested that addition of nanosized silicon and aluminum oxide particles to an aqueous suspension of clays both in the natural and in the dehydrated (thermally activated) state could cause structural changes in redistribution of the particles of the suspension itself and formation of new structural forms. The mechanism of their action can be identical to the effect of traditional slip thinners, for example, liquid glass, or be subject to another scheme for modification of the structure of clay minerals.

Two clays were selected to study these processes: Nurlatskoe bentonite and Nizhneuvel'skoe refractory clay; their compositions are reported in Table 1.

The selected clays were used in natural (25°C) and thermally activated (heating to 380°C, holding for 2 h, and abruptly cooling in a freezer) states, ground, and passed through a sieve with a 1-mm hole diameter.

Silica sol (SS) with a particle diameter of 8 nm and pH 9.9, aluminum hydrosol (AS-1) with the structure of a crystallite of the boehmite type 3.5 – 4 nm in diameter and pH 4 were used as the nanodisperse particles. The nanosols were synthesized at Kazkhim NII Co.

The silicon oxide sols are lyophilic colloidal systems with nanosized particles, usually of spherical shape. The surface of the nucleus of the colloidal particle, consisting of silicon dioxide, SiO_2, is covered with silanol groups, SiOH, whose dissociation causes the appearance of an electric double layer and negative charging of the sol particles:

$$\equiv SiOH + {}^{-}OSi \equiv \; \rightarrow OH^{-} + \equiv Si - O - Si \equiv;$$

$$\equiv SiOH + {}^{-}OSi \equiv \; \rightarrow H_2O + \equiv SiO^{-}.$$

Formation of ring forms, cross-linking of the rings in parallel planes, and the appearance of bulky structures with subsequent growth to formation of a disperse silica particle take place at a low degree of polymerization. Stabilization of the colloidal system by addition of NaOH preserves the negative charges on the surface of the particles and prevents their aggregation.

The nanosized aluminum hydroxide hydrosols have the rhombic crystal structure of boehmite (γ-AlOOH). Air drying boehmite sol — xerogel — at 25°C can be dispersed again on addition of water. The studies of the structure of aluminum oxide xerogels by powder diffractometry and small-angle x-ray scattering showed that the aluminum oxide xerogel particles have a lamellar form and are 3.1 – 3.4 nm thick. According to the theoretical calculations, the boehmite crystals are formed by seven layers of γ-aluminum oxohydroxide. The studies were conducted in the Department of x-ray structural Studies at TsKP SATs at the Laboratory of Diffraction Methods Research Base of A. E. Arbuzov IOPC (Kazan').

The selected clays and distilled water were used to prepare 10%[3] aqueous suspensions as the basic compositions and suspensions with additives of 0.1% (over 100%) nanosols SS and AS-1. After standing for 24 h, the following parameters were determined in glass cylinders: pH of the solution, presence of sol and sediment.

After holding the suspensions for 24 h, samples of sols SS and AS-1 and sols and sediments in the investigated suspensions were studied in an Axioskop 40 optical polarizing microscope (Figs. 1 and 2).

The results of the studies showed that both clays in the natural state (25°C) with no additives and with nanosol additives SS, then AS-1 caused a 2 – 2.5% increase (swelling) in the sediment and the same pH of the solution (5 – 6). The pH of the solution only decreased for the refractory clay, while it did not change for the bentonite clay. This could be due to substitution of interpacket water by particles of SS nanosol at active OH groups with subsequent addition of particles of AS-1 identical to the packet structure of laminar crystals of clay minerals. This effect should be greater in the refractory clay due to the presence of kaolinite, which also shows a change in the pH of the solution. The reverse order of addition of SS and AS-1 does not have a similar effect, which can also be explained by the difference in the crystal structures of montmorillonite and kaolinite.

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[3] Here and below — content by weight.
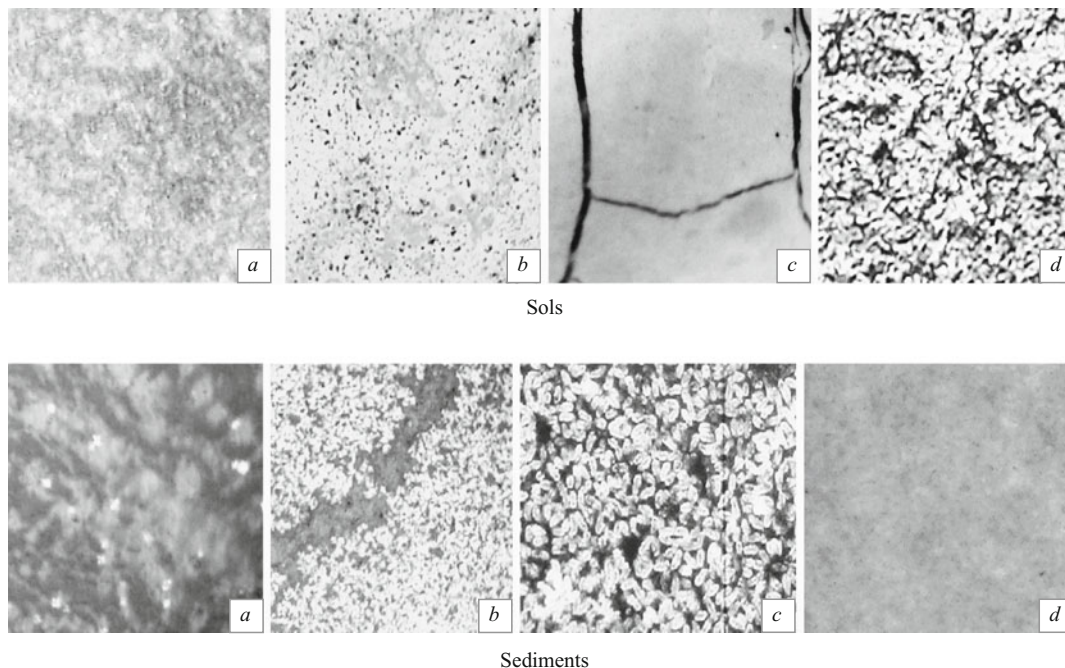
Fig. 1. Microstructures of disperse phases (sols and sediments) of 10% aqueous suspensions of diatomite (*a*), thermally activated (380°C) bentonite clay (*b*), ground quartz (*c*) with 0.1% silica sol (SS) (*d*), thermally activated (380°C) bentonite clay with 0.1% SS and 0.1% AS-1. × 500. Reflected light.
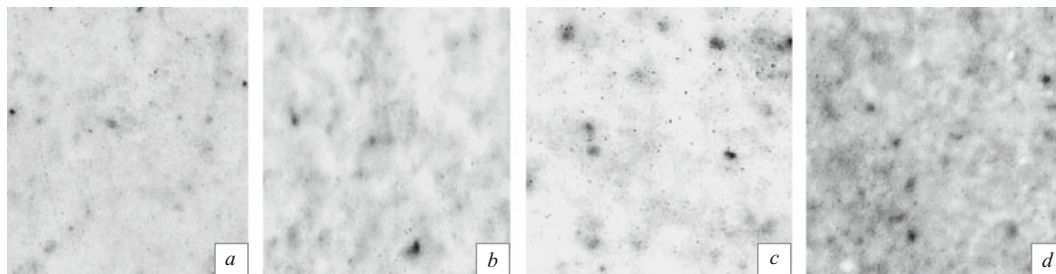

Fig. 2. Microstructures of disperse phases (sols and sediments) of 10% aqueous suspensions of diatomite (*a*) and refractory clay (*b* – *d*) modified with SS and AS-1 nanosols. × 500. Reflected light: *a*) Diatomite + 0.1% SS (sediment); *b*) refractory clay + 0.1% SS (sediment); *c*) thermally activated refractory clay (380°C) + 0.1% SS (sol); *d*) thermally activated refractory clay (380°C) + 0.1% SS + 0.11% AS-1 (sediment).

Thermal activation of the clays at 380°C removed most of the interpacket water, increasing the activity of free OH groups in the minerals [6].

The thermally activated bentonite clay in the suspension exhibited formation of stable sol and an increase in the pH of the solution by 1. Sol did not form in the suspension of refractory clay, while the pH of the solution decreased by 1. This could be due to removal of some of the silicon-oxygen tetrahedrons or their associates from the crystal structure of the montmorillonite with formation of silica sol, which should increase the pH. This was also observed in the suspension of thermally activated bentonite clay, and the surface of the silica particles can inherit the character of the surface of the cleft and in reacting with molecules of water, the api-

ces of the tetrahedrons become OH groups [9, 10, 11]. This effect should not occur and is not observed for kaolinite.

Addition of SS to suspensions of both thermally activated clays resulted in formation of stable sols and the pH decreased by 1. The products of sedimentation of ground quartz, diatomite with SS and AS-1 in water were examined to explain the observed effects (see Figs. 1 and 2). After standing for 24 h, formation of a stable sol whose particles activated in grinding was observed in the suspension of ground quartz with SS, and the modified SS form a structure of high dispersity, causing contraction in glass, and a series of drawn crystals 2 – 4 μm in size was formed in the sediment (see. Fig. 1). Diatomite exhibited the blurred structure of sol and sediment. The structure of the sol and sediment of
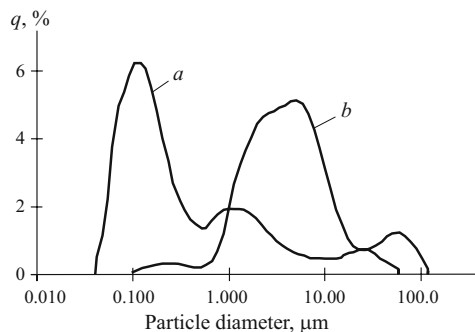
Fig. 3. Particle size distribution q in sols of 10% suspensions of thermally activated refractory (*a*) and bentonite (*b*) clays with 0.1% silica sol (SS) additive.

Fig. 4. Compressive strength of samples as a function of paste compositions and firing temperature: *1*) bentonite clay; *2*) bentonite clay + 0.1% SS + 0.1% AS-1; *3*) refractory clay; *4*) refractory clay + 0.1% SS + 0.1% AS-1.

Fig. 5. Dilution of clay suspensions in successive addition of nanosols: 0.1% SS + 0.1% AS-1 and 0.1% SS: *1*) 13% aqueous suspensions of bentonite clay; *2*) 40% aqueous suspensions of refractory clay.
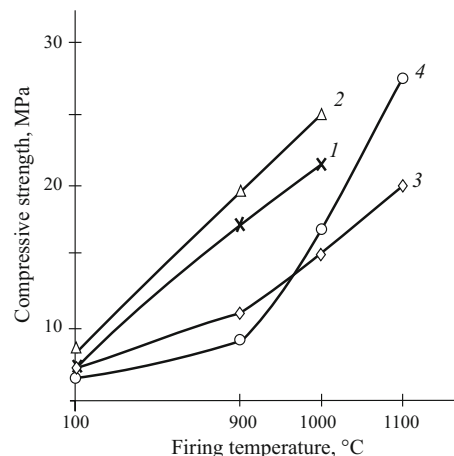
the thermally activated bentonite clay with SS occupied an intermediate position between them. With SS + AS-1, a sol close to the diatomite sol and quartz residue with respect to the granularity formed. With respect to the dispersity, the sediment of thermally activated clay with SS + AS-1 resembled a dense quartz sol. This composition in the molded and calcined samples exhibited the best strength indexes.

Figure 2 shows that the structures of the refractory clay with SS are identical to the structure of the lower part of the sediment of diatomite with SS, the structure of the sol of thermally activated refractory clay with SS, and the sediment of thermally activated refractory clay with SS + AS-1.

The analysis of the particle distribution in the sols of thermally activated clays with SS was performed on a HORIBA laser LA-950 V2 analyzer with a wavelength of 650 nm. Figure 3 shows that for the refractory clay, thermal activation and modification of SS resulted in a multifraction sol with the largest fraction of particles from 0.1 to 1.0 μm, and a single-fraction sol with a $1 - 10$ μm fraction for bentonite clay. The multifraction character of the refractory clay sol should cause better particle packing during drying and firing, and this in turn will be reflected in the properties of the final material, which is identical to the effect of HDBS [2].

Addition of SS and AS-1 successively to thermally activated clays did not result in formation of a stable sol but increased swelling of the sediment to the size of the unactivated clay. The pH of the solution decreased by 2 for the bentonite clay and increased by 2 units for the refractory clay. This could be due to filling of the interpacket space of the crystal structures of the minerals by particles of SS and AS-01 sol in place or partial substitution of water. These processes should be more effective for refractory clay due to the presence of active OH groups in kaolinite. Such structure formation of the material is manifested in the high shrinkage and compressive strength indexes for the samples of refractory clay (Fig. 4).

Changing the sequence of adding SS and AS-1 resulted in formation of a stable sol, the same pH of the solution and sediment for both clays, comparable to the indexes for the unmodified suspensions of thermally activated clays. This
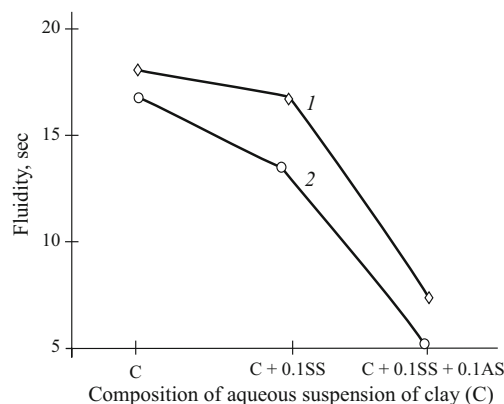
could confirm the previously advanced hypotheses concerning substitution of molecules of interpacket water by particles of nanosol.

The results of the study of the fluidity of aqueous suspensions of clays in modifying them with SS and AS-1 nanosols are shown in Fig. 5. The graph shows that for the refractory clay, the increase in the fluidity on addition of SS and consecutive addition of SS and AS-1 is greater than for bentonite clay, which is also in agreement with the previous arguments. A change in the hydration shells of the clay microparticles that affects the structure of the clay suspensions can take place simultaneously [2, 3].

Modification of clays with nanosols changed the shrinkage and strength of the samples formed from 50% clay slips of pure clays and modified with SS and AS-1. Modification decreased the shrinkage on drying and increased the shrinkage in heat treatment up to 900°C (to total elimination of

traces of OH groups and initial formation of mullite and crystobalite) [6]. Fig. 4 shows that the strength of the bentonite and refractory clays increases, while the strength of the refractory clay is an order of magnitude lower up to 900°C — the temperature above which exothermic rearrangement of the crystal lattice of Al_2O_3 due to an increase in the coordination of the aluminum ions begins [6]. The distribution of disperse phases in 10% thermally activated clays with SS taken on a HORIBA particle size distribution analyzer showed the presence of three fractions in the refractory clay sol in the size range primarily of 0.06 – 0.15 μm and 0.15 – 5.00 and 50.00 – 100.0 μm, and primarily a single fraction with a particle size of 5.00 to 50.00 μm. This should affect structure formation of the material in drying and firing, more favorably for refractory clay, and should also be reflected in the shrinkage, strength characteristics, and features of the final crystal structure of the material.

The studies showed that nanosols of aluminum and silicon oxides can be effective modifiers of structure formation of clay pastes for obtaining the necessary characteristics of ceramic slips which will increase the strength properties of fired articles. In addition, the use of nanosols, in contrast to the electrolytes used in slip technology (liquid glass, soda, etc.), does not introduced a significant amount of alkali metal ions in the paste, which would significantly affect sintering of the ceramic materials.

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